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RESEARCH ARTICLE

Structural effect of fluorophore on phenylboronic acid fluorophore/cyclodextrin complex for selective glucose recognition

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Abstract Based on the design of the fluorescent site of a fluorescent probe, we have created a unique system that changes its twisting response to sugar. Two probes were synthesized, in which phenylboronic acid and two kinds of aromatic fluorescent site (pyrene or anthracene) were conjugated by an amide bond. In the fluorescence measurement of pyrene-type probe **1**, dimer fluorescence was observed at high pH. In induced circular dichroism (ICD) experiments, a response was observed only in the presence of glucose and γ-cyclodextrin, and no response was seen with fructose. On the other hand, in the fluorescence measurement of anthracene-type probe **2**, dimer fluorescence was observed in the presence of both glucose and galactose, and the fluorescence was different from the case of fructose. When the ICD spectra of these inclusion complexes were measured, an inversion of the Cotton effect, which indicates a change in the twisted structure, was observed in galactose and glucose. These differences in response to monosaccharides may originate in the interaction between the fluorescent site and the cyclodextrin cavity.

Keywords sugar recognition, phenylboronic acid, cyclodextrin, fluorescence response, induced circular dichroism

1 Introduction

Monosaccharides play fundamental roles in various biological phenomena [1]. Among the many monosaccharides having similar structures in the human body, glucose is important as a diabetes biomarker [2,3]. To find or control diabetes, enzyme-type glucose sensors [4−6] have been developed to monitor blood glucose level. However, an artificial molecular sensor that shows selectivity for glucose is desired to overcome the drawbacks of enzyme-type sensors (low stability, poor thermal resistance, difficulty of use in nonphysiological conditions). In this regard, the development of a highly stable glucose sensor that is made of artificial molecules and functions in water is of considerable interest owing to its broad utility in food, cosmetic, and medicinal applications.

For monosaccharide recognition by artificial molecules, ester formation by the reaction of phenylboronic acid with the *cis*-diol moiety of sugar has been used widely [7]. Generally, phenylboronic acid shows fructose selectivity [8]. To achieve glucose selectivity, another substituent or a combination of two or more phenylboronic acid molecules is introduced [9,10]. Recently, polymer- [11−13], dendrimer- [14−16], or metal nanoparticle- [17−19] type artificial sensors that bind more than one recognition site have been developed.

We have been studying the formation of supramolecular inclusion structures using cyclodextrin (CyD) [20,21]. To realize the recognition of guest molecules in aqueous solution, CyD encapsulates hydrophobic probe molecules, thereby increasing fluorescence intensity due to molecular motion restriction within the clathrate structure. Through this encapsulation, the guest molecule is recognized from a wavelength shift in the fluorescence spectra due to the formation of dimers, or a change in the induced circular dichroism (ICD) spectra, which is due to the interaction

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between the chiral field of CyD and the absorption band of the probe molecule.

We have investigated ICD response in a system in which a phenylboronic acid type azo probe is included in CyD [22,23]. By introducing an amino group to the hydroxyl group of γ-CyD, we have developed a supramolecular system for the multipoint recognition of glucose using fluorescence measurement of a system combining a pyreneboronic acid probe [24,25]. Based on these findings, we aimed to investigate the structure of the fluorescent moiety on the multipoint sugar recognition function, using a system in which two fluorescent phenylboronic acid probes are included in γ-CyD.

2 Materials and methods

2.1 Reagents and chemicals

1-Aminopyrene, 2-aminoanthracene, 4-carboxyphenylboronic acid, 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzoic acid, and β- and γ-cyclodextrins were obtained as special-grade reagents from Wako Pure Chemical Industries Ltd. (Osaka, Japan). 4-(4,6-Dimethoxy-1,3,5-triazin-2-yl)-4-methyl morpholinium chloride (DMT-MM) was purchased from Kokusan Chemical Co., Ltd. (Tokyo, Japan). Acetonitrile, chloroform, methanol, and dimethylsuloxide-d_6 were purchased from Kanto Chemical Co., Inc. (Tokyo, Japan). All other organic solvents, monosaccharides, and reagents were commercially available with guaranteed grade and used as received. Water was doubly distilled and deionized by a Milli-Q water system (WG222, Yamato Scientific Co., Ltd. Tokyo, Japan and Autopure WR-600G, Merck Millipore, MA, USA) before use.

2.2 Apparatus

^{1}H nuclear magnetic resonance (NMR) spectra were measured with a JNM-ECX500 (JEOL Ltd. Tokyo, Japan) at 300 K. pH values were recorded using a Horiba F-52 pH meter (Horiba, Ltd., Kyoto, Japan). Ultraviolet-visible (UV-vis) absorption spectra were measured using a Hitachi U-3900 UV-vis spectrophotometer (Hitachi High-Technologies, Co., Tokyo, Japan) equipped with a Peltier thermocontroller and a 10 mm quartz cell. A quartz cuvette with 1.0-cm path length was used. ICD spectra were obtained with a J-820 spectrophotometer (Jasco Corp., Tokyo, Japan) using a 10 mm quartz cell. The scan speed was 120 nm·min^{-1}. Fluorescence spectra were measured using a HITACHI F-4500 or F-7000 fluorescence spectrophotometer (Hitachi High-Technologies, Co., Tokyo, Japan) equipped with a 10 mm quartz cell.

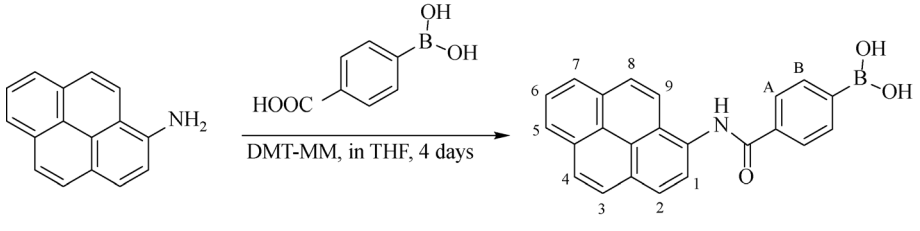
2.3 Synthesis of probes

2.3.1 Synthesis of pyrene-type probe **1**

Pyrene-type probe **1** ((4-(pyren-1-yl-carbamoyl)phenyl) boronic acid) was synthesized, as shown in Scheme 1. 1-Aminopyrene (0.441 g, 1.99 mmol) and 4-carboxyphenylboronic acid (0.335 g, 2.02 mmol) were dissolved in 20 mL of methanol in a 100 mL Erlenmeyer flask. DMT-MM (1.01 g, 3.22 mmol) was added into the flask, and the reaction mixture was stirred for 2.5 h at room temperature. The color of the reaction mixture changed from dark green to white and the solution was suspended. The reaction mixture was filtered through a membrane filter. The filtrate was washed with methanol and dried *in vacuo* to give a gray solid (Yield 0.035 g, 4.5%). ^{1}H NMR (500 MHz, DMSO-d_6) δ: 7.9–8.4 (pyrene, m, 9H), 7.98 (phenyl, d, 2H, 8.0 Hz), 8.12 (phenyl, d, 2H, 8.0 Hz), 10.8 (NH, s, 1H). ^{13}C NMR (125 MHz, DMSO-d_6) δ: 122.94, 123.80, 124.36, 124.89, 125.10, 125.15, 125.32,,125.65, 126.42, 126.77, 126.92, 127.19, 127.23, 128.94, 130.48, 130.75, 131.85, 134.10, 136.68, 166.45. ESI-TOF-MS (solvent: MeOH) m/z = 392 (M-3H$^+$+ 2CH$_3$: Methyl ester formation of phenylboronic acid could occur in ionization process of ESI-TOF-MS)$^-$. Anal. Calcd for $C_{23}H_{16}NO_3B$ (%): C, 75.64; H, 4.42; N, 3.84. Found: C, 75.70; H, 4.82; N, 3.74.

2.3.2 Synthesis of anthracene-type probe **2**

Antharacene-type probe **2** ((4-(anthracen-2-yl-carbamoyl) phenyl)boronic acid) was synthesized, as shown in Scheme 2. A solution of 2-aminoanthracene (0.773 g, 4.0 mmol) was dissolved in 50 mL of tetrahydrofuran (THF). 4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)benzoic acid (0.996 g, 4.0 mmol) was dissolved in 50 mL of THF. Then, these two solutions were mixed in a 300 mL



Scheme 1 Synthesis of pyrene-type probe **1**.

Erlenmeyer flask, and DMT-MM (1.90 g, 6.0 mmol) was added. The reaction mixture was sonicated. THF was added to make 200 mL, and the reaction mixture was stirred for 7 days at room temperature. The reaction was monitored by TLC. The solvent was evaporated and the residue was dissolved in chloroform. This solution was washed with water twice and dried using $MgSO_4$. The crude solution was purified by recycling preparative HPLC (LC-810, Japan Analytical Industry Co., Ltd., Tokyo, Japan). To remove the protective group, the 2nd fraction was dissolved in 150 mL of an acetonitrile-water mixture (2:1 (v/v)), and the reaction mixture was stirred for 7 days at room temperature in the dark. The solvent was removed *in vacuo* to obtain yellow crystalline solid (Yield: 39.2 mg, 2.9%). ^{1}H NMR (500 MHz, DMSO-d_6) δ: 7.48 (H5, H6, m, 2H), 7.87 (H1, dd, 1H), 7.87 (HA, HB, dd, 4H), 8.07 (H2, H4, H7, m, 3H), 8.38 (B-OH, s, 2H), 8.48 (H3 or H8, s, 1H), 8.51 (H3 or H8, s, 1H), 8.66 (H9, broad s, 1H), 10.49 (NH, s, 1H). ^{13}C NMR (125 MHz, DMSO-d_6) δ: 115.82, 122.35, 125.58, 125.73, 126.17, 126.36, 127.14, 128.27, 128.60, 129.12, 129.22, 131.07, 132.06, 132.20, 134.58, 136.64, 136.77, 166.59. Anal. Calcd for $C_{21}H_{16}NO_3B$(%): C, 73.93; H, 4.73; N, 4.11. Found: C, 73.79; H, 4.82; N, 3.96.

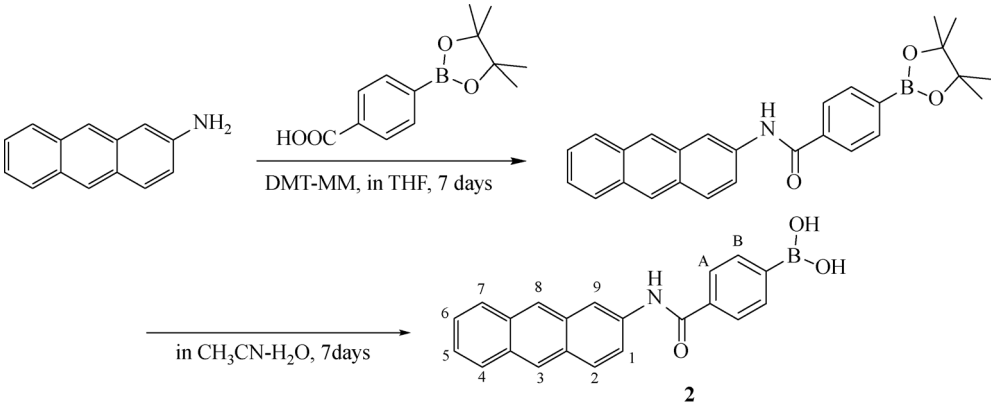
3 Results and discussion

3.1 Evaluation of pyrene-type probe **1**

Fluorescence spectral changes with pH of pyrene-type probe **1** included in β-CyD are shown in Fig. S6. Considering the cavity size of β-CyD, it was hypothesized that probe **1** and β-CyD would form a complex in the substance ratio of 1:1. As pH increased, the fluorescence intensity around 370 nm increased slightly, whereas that around 430 nm decreased markedly. The fluorescence emission around 370 nm was enhanced because the photoinduced electron transfer from pyrene to phenylboronic acid accompanying the anionization (addition of a hydroxyl group) of phenylboronic acid was suppressed. On the other hand, the emission near 430 nm was dependent on the dissociation of the amino group [26], which is considered to be irrelevant to the ester formation in the reaction of phenylboronic acid with a monosaccharide molecule. As this behavior does not depend on the type of monosaccharide, this inclusion complex is considered to have no sugar recognition function, and is therefore unsuitable for use as a monosaccharide sensor.

In the inclusion complex with γ-CyD, which has a larger cavity than β-CyD, a different behavior from that of β-CyD was noted. The pH dependence of the fluorescence spectra in the presence of various monosaccharides is shown in Fig. 1. When pH was raised to approximately 12, the fluorescence intensity around 500 nm was markedly enhanced only in the case of glucose solution. This fluorescence enhancement originates in the dimer fluorescence due to the proximity of the two pyrene molecules in γ-CyD, and it is considered that an approximately 2:1 complex formation occurs only in glucose solution. Therefore, we investigated the fluorescence intensity changes with the addition of various sugars to the **1**/γ-CyD complex. The plots of fluorescence intensity change at 496 nm versus sugar concentration are shown in Fig. 2. As a result of the 1:2 complex formation of glucose and probe **1**, the dimer fluorescence intensity increased with increasing sugar concentration. On the other hand, no dimer formation was observed with the other sugars.

The dimer formation of glucose observed in the fluorescence spectrum was also confirmed by the UV-Vis spectra. When various sugars were added to **1**/γ-CyD inclusion complex at pH 11.3, no difference was noted between without sugar, with fructose, and with galactose. However, the peak around 350 nm became broad and clear red-shift was observed only when glucose was added (Fig. 3(a)). This red-shift is ascribed to the *j*-association of pyrene [27,28]. That is, two molecules of **1** was not parallel dimer but in the state of diagonal dimer in the γ-CyD



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Scheme 2 Synthesis of anthracene-type probe **2**.

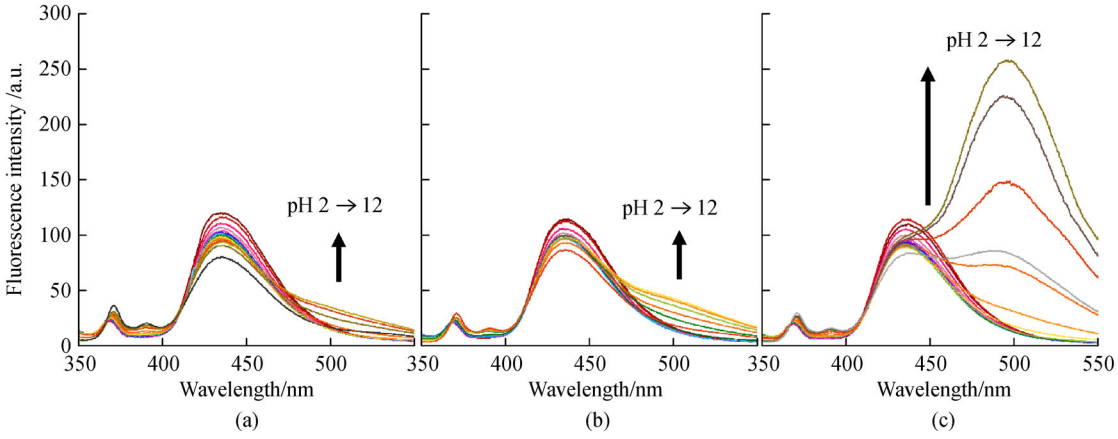

Fig. 1 pH dependence of fluorescence spectra for **1**/γ-CyD in 2% DMSO–98% water (*v*/*v*), (a) without sugar, (b) in 30 mmol·L^{-1} fructose, and (c) in 30 mmol·L^{-1} glucose. [**1**] = 1.0 ×10^{-5} mol·L^{-1} in 2% DMSO–98% water (*v*/*v*), [γ -CyD] = 5 mmol·L^{-1}, pH adjusted with 0.01 mol·L^{-1} phosphate buffer, at 25°C, *I* (ionic strength) = 0.1 mol·L^{-1} with NaCl, λ_{ex} = 328 nm.

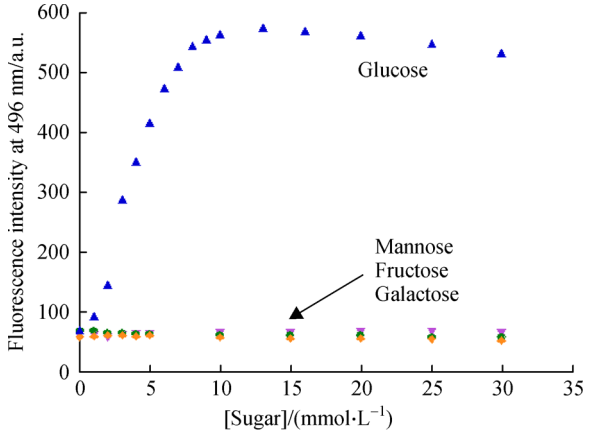

Fig. 2 Fluorescence intensity changes at 496 nm for **1**/γ-CyD versus sugar concentration in 2% DMSO–98% water (*v*/*v*). [**1**] = 1.0 × 10^{-5} mol·L^{-1} in 2% DMSO–98% water (*v*/*v*), [γ-CyD] = 5 mmol·L^{-1}, pH adjusted to 11.3 with 0.01 mol·L^{-1} Na_2CO_3 buffer, at 25°C, *I* = 0.1 mol·L^{-1} with NaCl, λ_{ex} = 328 nm.

cavity. When the UV-Vis spectrum was measured by addition of glucose, the red-shift increased with the glucose concentration increased exhibiting a clear isosbestic point (Fig. 3(b)). This is an additional evidence that the addition of glucose promotes dimer formation of **1** in the γ-CyD cavity.

In order to investigate the inclusion structure of this complex, ICD spectral measurement was carried out under sugar addition conditions at pH 11.3. The results are shown in Fig. 4. A complex split-type Cotton effect was observed only in the case of glucose. This split-type Cotton effect, which shows in the twisted structure of two molecules with the same dipole moment in the chirality of CyD [28−32], indicates the inclusion of two probe **1** molecules in the CyD cavity. On the other hand, almost no ICD response to galactose and fructose was observed. The positive Cotton effect observed around 260–280 nm is a result of the chirality of D-fructose itself.

From these results, we considered that the probe formed an inclusion structure, as shown in Fig. 5.

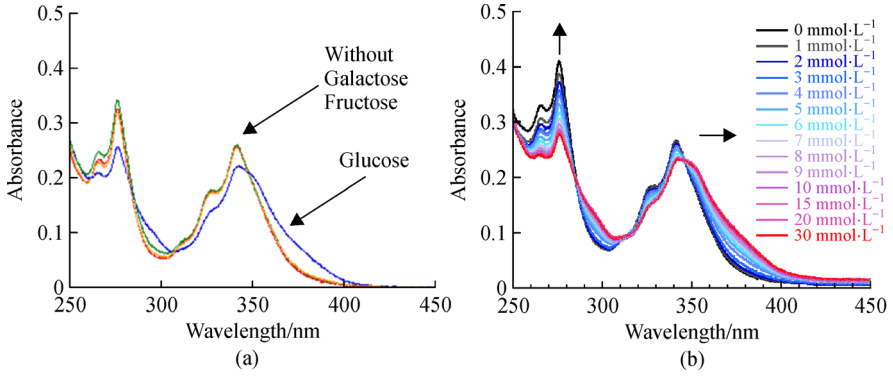

Fig. 3 (a) UV-Vis spectra without sugar or in 30 mmol·L^{-1} monosaccharides and (b) UV-vis spectral change with addition of glucose (b) for **1**/γ-CyD in 2% DMSO–98% water (*v*/*v*). [**1**] = 1.0×10^{-5} mol·L^{-1}, [γ-CyD] = 5 mmol·L^{-1}, pH adjusted to 11.3 with 0.01 mol·L^{-1} Na_2CO_3 buffer, at 25°C, *I* = 0.1 mol·L^{-1} with NaCl.

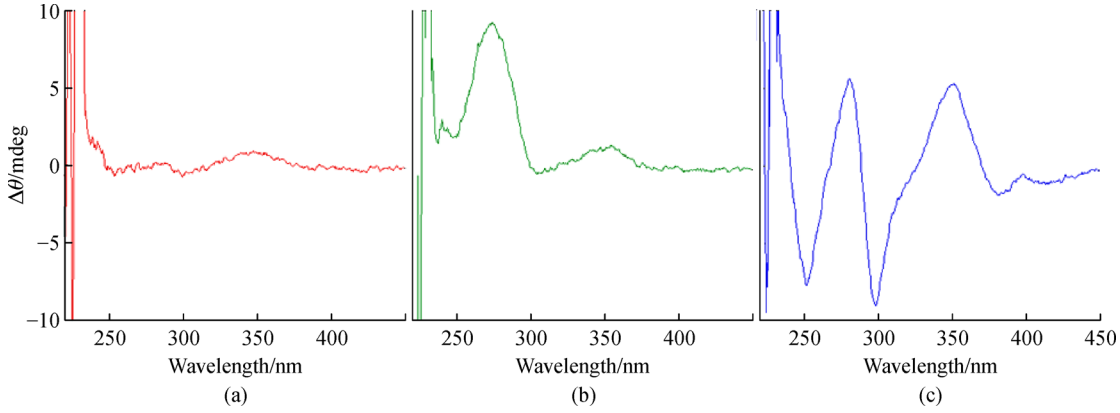

Fig. 4 ICD spectra for **1**/γ-CyD in 2% DMSO–98% water (*v*/*v*), (a) without sugar, (b) in 30 mmol·L^{-1} fructose, and (c) in 30 mmol·L^{-1} glucose. [**1**] = 1.0 × 10^{-5} mol·L^{-1}, [γ-CyD] = 5 mmol·L^{-1}, pH adjusted to 11.3 with 0.01 mol·L^{-1} Na_2CO_3 buffer, at 25°C, I = 0.1 mol·L^{-1} with NaCl.

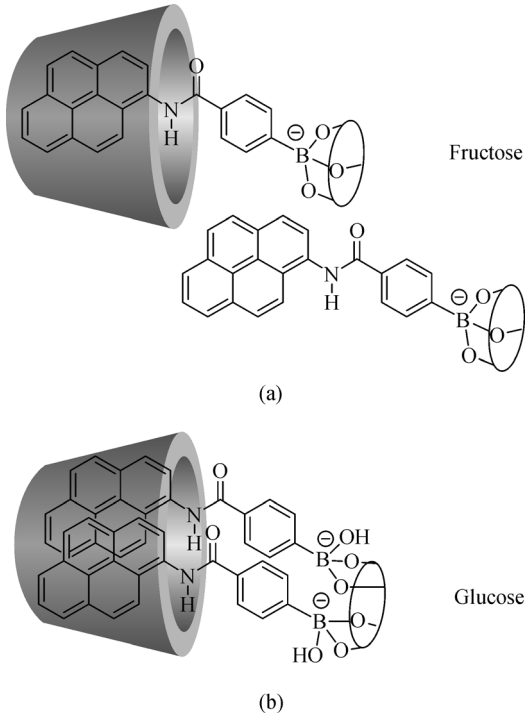

Fig. 5 Estimated structures of **1**/γ-CyD inclusion complexes with (a) fructose and (b) glucose.

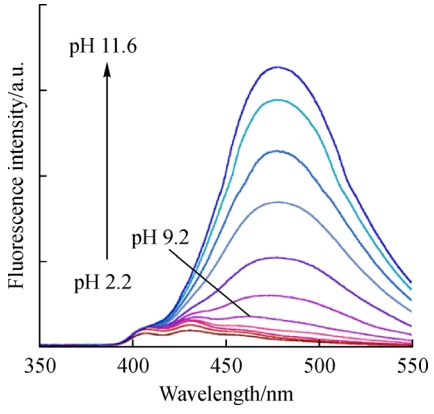

Fig. 6 pH dependence of fluorescence spectra for **2**/γ-CyD in 2% DMSO–98% water (*v*/*v*), in 30 mmol·L^{-1} glucose. [**2**] = 5.0 × 10^{-6} mol·L^{-1}, [γ-CyD] = 5 mmol·L^{-1}, pH adjusted with 0.01 mol·L^{-1} phosphate buffer, at 25°C, I = 0.1 mol·L^{-1} with NaCl, λ_{ex} = 325 nm.

3.2 Evaluation of anthracene-type probe **2**

Anthracene-type probe **2** has a different fluorescent site from probe **1**. We investigated the pH dependence of the fluorescence spectra for the **2**/γ-CyD inclusion complex (**2**/γ-CyD) in the presence of glucose in aqueous solution. The results are shown in Fig. 6. Fluorescence enhancement by dimer formation was observed in the alkaline condition, similar to the case of the **1**/γ-CyD complex. Therefore, fluorescence spectral changes of the **2**/γ-CyD complex with the addition of monosaccharides were examined at pH 11.0. The plots of dimer fluorescence change versus saccharide concentration are shown in Fig. 7. Unlike pyrene-type probe **1**, the **2**/γ-CyD inclusion complex exhibited dimer emission even without sugar in the alkaline condition. When various monosaccharides were added to the **2**/γ-CyD inclusion complex, the dimer fluorescence was enhanced or decreased. Interestingly, galactose showed the strongest dimer fluorescence enhancement, followed by glucose. In contrast, when fructose, sorbitol or mannose was added, the dimer fluorescence decreased due to 1:1 formation with these sugars. Therefore, it is considered that one molecule was released from the original dimer complex included in γ-CyD. In pH dependence measurement of UV-vis spectra, the peak around 350 nm became broad and clear red-shift was observed in alkaline pH region when glucose was

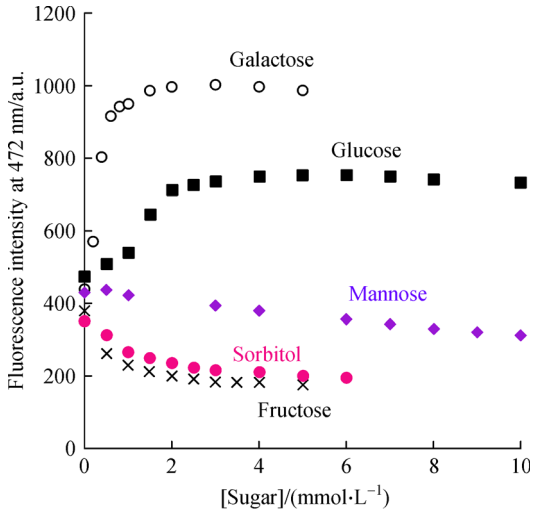

Fig. 7 Fluorescence intensity changes at 472 nm for **2**/γ-CyD versus sugar concentration in 2% DMSO–98% water (*v*/*v*). [**2**] = 0.5×10^{-5} mol·L^{-1}, [γ-CyD] = 5 mmol·L^{-1}, pH adjusted to 11.0 with 0.01 mol·L^{-1} Na_2CO_3/$NaHCO_3$ buffer, at 25°C, I = 0.1 mol·L^{-1} with NaCl, λ_{ex} = 325 nm.

added (cf. Electronic Supplementary Material, ESM; Fig. S8).

ICD spectral changes of the **2**/γ-CyD complex with increasing sugar concentration at pH 11.0 are shown in Fig. 8. In the case of glucose addition, an inversion of orientation to the original split-type Cotton effect was observed. In the case of galactose addition, the split-type Cotton effect was enhanced in the same direction. This difference is due to a variation in the angle of ester formation in the reaction of phenylboronic acid with glucose and galactose, and the phenomenon of twist inversion at the time of glucose addition was observed. The same ICD spectral sign for galactose and without sugar suggests that this probe shows galactose selectivity in the absence of a template. This phenomenon is similar to that reported by us in the gelation using phenylboronic acid azo probe [11]. On the other hand, the original split-type Cotton effect decreased with fructose addition. This decrease is a result of the collapse of the 2:1 inclusion structure, because fructose and probe **2** form an anionic ester in 1:1 ratio. This is consistent with the results of fluorescence measurements.

From these results, we found that the structure of the inclusion complex was markedly changed by its response to monosaccharides. The estimated inclusion formation is shown in Fig. 9. The fluorescence and ICD responses were noticeably changed by temperature (cf. ESM). When the temperature was increased, the signals were attenuated because the supramolecular formation was weakened by thermal motion.

4 Conclusions

We have developed a phenylboronic acid type probe/γ-CyD inclusion complex that fluoresces in the presence of sugar in aqueous solution. The phenylboronic acid type probe/γ-CyD inclusion complex functions as a multipoint-recognition sugar sensor whose fluorescence intensity is increased by the formation of a 2:1 complex. Based on various measurements of fluorescence and ICD spectra, we revealed that the differences in sugar selectivity depend on the structure of the fluorescent moiety.

However, the pH range for sugar recognition is limited to the alkaline region, and the pH condition is unsuitable for the measurement of biological substances or bio-related substances. To overcome these disadvantages, we are investigating probe designs and performing more experiments.

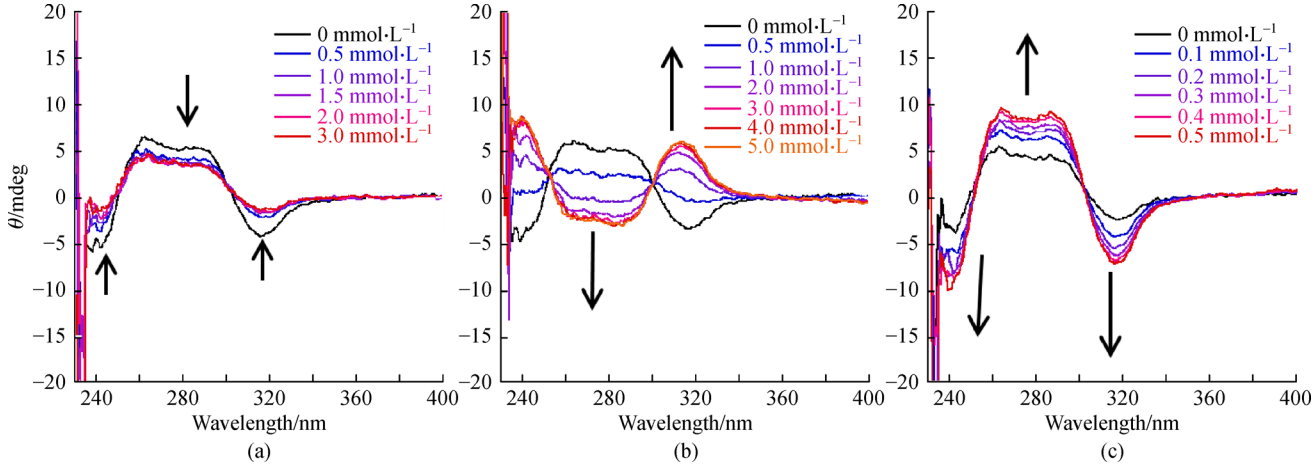

Fig. 8 ICD spectral changes of **2**/γ-CyD in 4% DMSO–96% water (*v*/*v*) with (a) fructose, (b) glucose, or (c) galactose. [**2**] = 1.0×10^{-5} mol·L^{-1}, [γ-CyD] = 5 mmol·L^{-1}, pH adjusted to 11.0 with 0.01 mol·L^{-1} Na_2CO_3 buffer, at 25°C, I = 0.1 mol·L^{-1} with NaCl. [Sugar] = 0–5.0 mmol·L^{-1}.

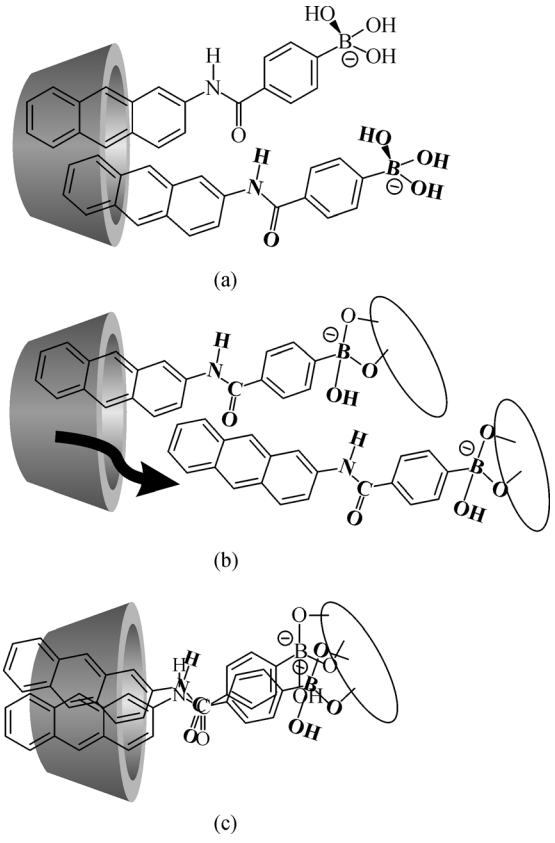

Fig. 9 Estimated structures of **2**/γ-CyD inclusion complex (a) with/without sugar, (b) with fructose/mannose, and (c) with glucose/galactose.

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